

A comparative study of alkali activated slag cement concretes with carbonates and silicate activators.

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Abstract Alkali-activated cements are increasingly gaining interest as viable alternatives to Portland cement, because they are considerably reducing CO₂ emissions compared to traditional Portland cements while maintaining or exceeding performance requirements commonly specified for construction applications. Experience of this type of cement shows that the results are very sensitive to mixing procedures and curing conditions. This article thus studies concretes with Na₂CO₃ activated ground granulated blast furnace slag (GGBS) cement mixes and mixes of on Na₂CO₃ plus Na₂SiO₃ activated GGBS under different mixing and curing regimes. After studying different mixing procedures of the ingredients and their effects on the compressive strength, the most suitable mixing procedures were adopted for a series of mechanical and durability related tests using different curing conditions. The results showed that providing the carbonate in solution rather than powder form, resulted in higher strengths. Curing conditions at ambient temperature and high humidity regimes were most successful in maintaining strength development in time. All mixes had adequate strengths for structural concrete but those with Na₂SiO₃ developed the highest strengths at all ages and curing conditions.

Keywords: concrete sustainability; alkali-activated cements; sodium carbonate; ground granulated blast furnace slag; industrial waste management

1. Introduction

In the context of engineering sustainability, alkali-activated cements (AAC), have been increasingly attracting attention worldwide. These cementitious binders are free of Portland cement (PC), whose production is energy-intensive and responsible for 5-10% of global anthropogenic CO₂. They are thus claimed to have a much smaller environmental footprint than PC, linked to their lower embodied energy and elimination of CO₂ emissions from clinker calcination (Jamieson et al, 2015). These binders consist of an aluminosilicate precursor, which can be a natural or industrial waste material, activated by a soluble substance that can supply alkali metal ions (hydroxides, carbonates, sulphates, aluminates, or oxides). This raises the pH of the mixture and accelerates the dissolution of the solid precursor. Additional advantages

are linked to the use of by-product or waste materials, reducing the need of landfilling or of quarrying virgin material, thus leading to considerable energy savings overall.

A number of researchers estimated the advantages of using AAC compared to PC, in terms of environmental impact. Davidovits (2013) mentioned that geopolymers, a type of AAC could potentially reduce CO₂ emissions by up to 5-6 times. Yang et al., (2013) evaluated the CO₂ reduction of AAC concrete with alkali-activated ground granulated blast-furnace slag (GGBS), from the cradle to pre-construction. Performance efficiency indicators, binder and CO₂ intensities, showed that the contribution of the binder to the total CO₂ emission is more significant in PC-based concrete than in AAC concrete, for which the contribution of aggregate transportation is more critical. Overall, a reduction of 55%-75% CO₂ emission of AAC concrete relative to PC concrete was estimated and a 20% CO₂ reduction rate in secondary precast concrete products that use alkali-activated GGBS binder instead of GGBS cement when the total aggregate-to-binder ratio ranged between 3.0 and 4.0. Finally, Ca(OH)₂-based AAC GGBS concrete showed a CO₂ intensity approximately 2.4 times lower than that of PC concrete. Salas et al (2018) performed a Life Cycle Assessment (LCA) of a geopolymer concrete, considering the most relevant raw materials and processes contributing to the environmental performance of these concretes and found that the Global Warming Potential (GWP) could be 64% lower than that of PC. Further reductions in the environmental impacts of cement production can be achieved by the use of waste materials in the AAC binder mixes. For instance, Passuello et al (2017) performed a life cycle analysis of an AAC produced from a kaolin sludge residue from the mining industry, and alkaline solutions derived from NaOH solutions and two different soluble silica sources, a commercial sodium silicate (waterglass), and chemically modified rice husk ash (RHA). They found that the use of locally available RHA-derived sodium silicate may reduce environmental impacts by more than 60% in 6 of the 9 categories assessed in the LCA and that using RHA-derived activators lowered the impacts compared to PC for 4 of the 8 categories evaluated, and led to a reduction of more than 70% in GWP. Jamieson et al (2015) determined the embodied energy of a geopolymer binder made from

fly ash and Bayer liquor, a waste stream from the processing of bauxite to alumina; they found that the derived geopolymer has an embodied energy of between 6 and 30% that of PC.

Yet, the most widely studied activators namely NaOH, Na₂SiO₃ and their combination are expensive and suffer from other disadvantages such as rapid hardening, resulting in difficulty to cast, and are very caustic, causing health and safety concerns during their handling. In addition, unless derived from some waste material as recently proposed (see e.g., Tchakouté et al. 2016, Passuelo et al, 2017), they may also require high energy input for their production.

In view of the above, sodium carbonate has been identified as a suitable alternative activator, with the advantage of being more cost-effective and environmentally friendly than other widely used activators; it can be obtained as a secondary product from industrial processes, or by mining alkali carbonate deposits, followed by moderate-temperature thermal treatment (Bernal et al, 2016). It is less caustic, due its lower pH compared to hydroxides, which may result in low early strengths but in the long term, considerable strength gains are observed, due to the formation of carbonated compounds. The use of Na₂CO₃ as an activator of industrial slags was adopted in the former Soviet Union. Studies on slag concretes, activated by carbonates or carbonate/hydroxide mixtures that were cast between 1964 and 1982, showed that these concretes demonstrated very good durability under conditions in which Portland cements would have deteriorated rapidly; they also showed strength gains over their service life (Xu et al, 2008). Yet, there is a very limited international literature in English on these AAC systems (see e.g., Li et al. 2000; Bernal et al., 2015 and 2016; Kovtun et al., 2015; Abdalqader et al. 2016); the available papers focus mostly on cement or mortar mixes rather than concrete with Na₂CO₃ AAC.

This paper thus presents research carried at London South Bank University, focusing on concrete mixes based on Na₂CO₃ cement or Na₂CO₃-Na₂SiO₃ cement mixes. The scope of the paper is to present comparative results of salient mechanical and durability properties, considering the effect of mixing and curing conditions. The reason for this is that literature on AAC has shown that the results are highly dependent on the mixing sequence/ procedure and mixing time (Bernal et al., 2014), as well as the curing conditions. In the presented research, the effect of these factors on these little researched systems was studied. Here, a summary of the main findings is presented.

2. Materials and methods

The precursor used in the AA binder mixes was GGBS from Hanson Regen. GGBS was provided by Hanson Regen; its suitability for AAC and chemical composition were discussed in Mavroulidou and Martynková (2018). The analytical grade alkali activators supplied by Fisher Scientific were sodium silicate Na₂SiO₃ solution of a modulus $M=SiO_2/NaO_2=2$ and anhydrous sodium carbonate pellets ($\geq 99\%$ purity). Aggregates used were river sand of 5mm maximum size and gravel of 10 mm maximum size. The concrete mixes used are shown in

Table 1. For consistent comparisons, all mixes had the same liquid/solid ratio.

The investigation started with duplicate cubes to observe comparatively the effect of the mixing procedure and time on the setting behaviour, workability, and 7-day compressive cube strength of the AAC. The mixing considered (a) supplying Na₂CO₃ as a powder versus solution; (b) a number of combinations in the sequence of mixing the different ingredients, i.e., aggregates, precursor, water and activators; these aren't detailed here for the sake of brevity. An extended length of mixing time was also provided, as recommended in RILEM (2014) for AAC. Based on the first set of tests, the best mixing procedure was then followed for the complete set of tests of the mixes with Na₂CO₃ only and Na₂CO₃+Na₂SiO₃, respectively.

The compressive strength of the concrete mixes at different curing times was then assessed. In addition to this, a number of tests relevant for the durability of the concrete were performed, namely: absorption by immersion and by capillary rise, and effective porosity of the specimens using a helium porosimeter apparatus.

Table 1. Details of mix design (kg/m³)

Mix ID	GGBS	Sand	Coarse aggregate	Na ₂ CO ₃ Powder	Na ₂ SiO ₃	Added Water	l/s
Mix1a (Na ₂ CO ₃ powder)	415	784	1089	37	0	249	0.55
Mix1b (Na ₂ CO ₃ solution)	415	784	1089	37	0	81	0.55
Mix2a (Na ₂ CO ₃ powder + Na ₂ SiO ₃ solution)	415	784	1089	18.5	4625	22125	0.55
Mix2b (Na ₂ CO ₃ solution + Na ₂ SiO ₃ solution)	415	784	1089	18.5	4625	13725	0.55

*l/s: liquid/solid ratio; it includes water and solids in activator solutions

For each mix four different curing methods were studied: (a) Method 1: curing in moulds at room temperature for 72h, demoulding and water-curing at 20°C, until required for testing; (b) Method 2: constant humidity curing, where samples were kept in moulds and covered by an impermeable membrane to preserve their original moisture content; (c) Method 3: curing at 65°C for 5.5 hours, then, after cooling overnight, demoulding and water-curing at 20°C; (d) Method 4: high humidity curing i.e., at a relative humidity of 95% and a temperature of 25°C (Mavroulidou and Shah, 2021).

3. Results

The first test of results investigated the effect of the mixing procedure. The results showed that providing the carbonate

in solution rather than in powder form resulted in higher strengths for both Mixes 1 and 2. They also indicated the sequence of mixing to follow for best concrete outcomes. This consisted in mixing for 5 minutes at each stage, where new materials were introduced in the mix, followed by some resting period. The subsequent detailed investigation thus followed this implementation and mixing procedure. The most salient findings of the detailed investigation, in terms of average values of each property, are summarised in Table 2. All mixes showed good compressive strengths, adequate for structural concrete, although mixes containing also Na₂SiO₃ resulted in higher strengths. The latter mixes showed however more problems with hardening and in some sets of specimens were still too soft after 72h from casting.

Table 2. Summary results: strength, absorption, porosity

MIX ID	Curing Method	Compressive Strength (MPa)		Absorption (%)	porosity (%)
		7 days	28 days	I:immersion C:capillary	28 days
Mix1	1	23	40	7.6(I); 83(C)	14.2
	2	21	39	7.8(I); 7.8(C)	14.1
	3	30	37	6.9(I); 7.3(C)	11.4
	4	32	44	7.7(I); 8.2(C)	11.1
Mix2	1	36	62	7.3(I); 9.2(C)	14.1
	2	38	62	7.4(I); 9.0(C)	13.9
	3	49	54	5.9(I); 9.2(C)	14.9
	4	44	58	7.7(I); 8.7(C)	14.1

The effect of curing method on the strength was variable; for early strengths, the two best curing methods were 4 (high humidity) or 3 (temperature); this is consistent with observations on different AAC mixes without Na₂CO₃ activator (see e.g., Mavroulidou and Shah, 2021 or Mavroulidou and Martynková, 2018). However, for the 28-day strength, i.e., the nominal strength used for concrete design, method 3 led to limited further strength development in comparison with methods that provided higher exposure to moisture at all curing times; interestingly, method 1, had the highest strength development in time despite possible alkali ion leaching into the water.

Method 3 mixes showed generally the lowest water absorption with one exception. This is consistent with Bakharev et al. (1999), who attribute this to the reduced drying shrinkage, when thermal curing is used. Method 1 appears to give generally the highest absorption by capillary action but the second best for immersion, while mixes with Na₂SiO₃ had improved (lower) water absorption by immersion compared to mix with Na₂CO₃ only but a higher absorption by capillary rise; these observations are possibly linked to capillary pore size effects. The porosity results are variable and do not point at clear trends and links with the absorption results,

although in two instances the porosity of the Na₂CO₃ only mix was measured to be the lowest.

4. Conclusions

This paper studied concrete with Na₂CO₃ activated ground granulated blast furnace slag (GGBS) cement mixes and mixes of on Na₂CO₃ plus Na₂SiO₃ activated GGBS under different mixing and curing regimes. The rationale of the research was the potential further improvement in the sustainability of AAC upon addition of Na₂CO₃ in the cement mixes. The results showed that providing the carbonate in solution rather than powder form resulted in higher strengths. Curing conditions at ambient temperature and high humidity regimes were most successful in maintaining strength development in time, as with other AAC mixes reported in the literature. Overall, all mixes had adequate strengths for structural concrete although those including Na₂SiO₃ together with Na₂CO₃ developed the highest strengths at all ages and curing conditions. This shows promise that such AAC can be good alternatives Portland Cement concretes towards an increased sustainability in the construction sector.

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